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Crystal Growth of Molybdenum Oxides by Chemical Transport

Yoshichika BANDO*, Yasutoshi KATO**, and Toshio TAKADA**

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Single crystals of MoO_2, MoO_3, and Mo_nO_{3n-1} (n=4, 8, 9) were grown by chemical transport using $TeCl_4$ as transport agent. The electrical resistivities of the grown crystals were measured from liquid nitrogen temperature to room temperature.

I INTRODUCTION

There are many intermediate oxides such as Mo_nO_{3n-1} between MoO_2 and MoO_3. The phase diagram of the Mo-O system[1] showed that there are two distinct oxides, Mo_4O_{11} and Mo_9O_{26} between MoO_2 and MoO_3. Kihlborg[2] recognized five compounds as the intermediate oxides (Mo_nO_{3n-1}), that is, Mo_4O_{11}, Mo_5O_{14}, Mo_8O_{23}, Mo_9O_{26}, and $Mo_{13}O_{38}$, of which Mo_4O_{11} and Mo_9O_{26} are dimorphic. These intermediate oxides are the Magneli phases whose crystal structures can be described on the basis of the ReO_3 type.[2]

Chemical transport in the closed system has been applied to the growth of single crystal of the Magneli phases (V_nO_{2n-1}, Ti_nO_{2n-1}) using $TeCl_4$ as transport agent.[4~9] In crystal growth of Magneli phase, oxygen pressure is the important parameter which must be delicately adjusted to control the particular phase grown, becuase each phase is stable only in the narrow range of oxygen pressure. Authors[4~7] recently succeeded in growing single crystals of V_nO_{2n-1} and Ti_nO_{2n-1} by the chemical transport which had no need of the procedure of pressure control. The phase of single crystals (V_nO_{2n-1}) obtained by this method was all the same as that of source material. Therefore, it was considered that the single crystals of Mo_nO_{3n-1} were possible to be grown by the same method. We have much interested in the relation between the phase of source material and that of single crystals obtained.

II EXPERIMENTALS

Synthesis of source materials. Source materials for the chemical transport were synthesized from highly pure molybdenum dioxide and trioxide. Mixtures of MoO_3 and MoO_2 (3:1 in mole ratio) were pressed and placed in evacuated silica tube. The sealed tubes were heated at 550°C for 14 dyas in preparation of monoclinic Mo_4O_{11} and at 650°C for 5 days in preparation of orthorhombic Mo_4O_{11}.

* 坂東尚周：Laboratory of Inorganic Synthesis, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

** 加藤康敏，高田利夫：Laboratory of Solid State Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

The products were confirmed as a single phase by X-ray diffraction. Powders of Mo_8O_{23} and Mo_9O_{26} were prepared from MoO_3 and Mo_4O_{11}. The sealed tubes containing the mixture of MoO_3 and Mo_4O_{11} (4:1 in mole ratio) were heated at 700°C for 3 days in preparation of Mo_8O_{23}. The mixtures of MoO_3 and Mo_4O_{11} (5:1 in mole ratio) in the sealed tube were heated at 750°C for 2 days to product monoclinic Mo_9O_{26} and at 700°C for 3 days to product triclinic Mo_9O_{26}. These products were confirmed as a single phase by X-ray diffraction.

Chemical transport. The sealed tube for the chemical transport was prepared by the follows. Powder of molybdenum oxide (2 grams) was loaded at the end of transparent silica tube of 13 mm in diameter and 170 mm in length. $TeCl_4$ powder was added as transport agent into the silica tube. This procedure performed in a dry box to prevent $TeCl_4$ from deliquescence. After the tube was evacuated to 10^{-6} Torr, it was sealed off. The tube was kept in the horizontal electric furnace, where the source zone with the source material was heated at higher temperature and the crystallization zone at lower temperature. After the transport, the tube was quenched in water. In order to measure the transport rate, the crystals obtained at the crystallization zone were weighed.

Characterization of crystal. The crystals were identified by the X-ray powder method. Laue X-ray pictures were taken to confirm them to be single crystals. The measurement of electrical resistivity was carried out by means of four point method using a d.c. potentiometer.

III RESULTS

Table I shows the representative transport conditions for the growth of large

Table I

Source materials (2 grams)	Temperature gradient (deg/degC)	$TeCl^4$ (mg/cc)	Transport time (hr)	Transport rate (mg/hr)	Transported material	comment
MoO_2	700/630	3.0	70	10.3	MoO_2	reddish purple polyhedral
Mo_4O_{11} (ortho.)	690/640	3.0	70	26.4	Mo_4O_{11} (ortho.)	royal purple thin plate
Mo_4O_{11} (ortho.)	650/560	3.0	50	31.0	Mo_4O_{11} (monocli.)	royal purple thin plate
Mo_4O_{11} (monocli.)	580/500	3.0	50	26.6	Mo_4O_{11} (monocli.)	royal purple thin plate
Mo_8O_{23}	750/730	0.5	71	8.8	Mo_8O_{23}	purplish black
Mo_9O_{26} (monocli.)	770/760	0.5	69	6.1	Mo_9O_{26} (monocli.)	black
Mo_9O_{26} (monocli.)	770/745	0.5	70	16.7	Mo_9O_{26} (tricli.)	black needle
Mo_9O_{26} (tricli.)	750/730	0.5	70	13.8	Mo_9O_{26} (tricli.)	black needle
MoO_3	650/600	3.0	74	11.9	MoO_3	light yellow needle

crystals, the transport rate and the phases of obtained crystals. The composition of single crystals obtained was the same as that of source material. However, the phase of single crystals of Mo_4O_{11} and Mo_9O_{26} depended on the temperature of the crystallization zone, independently of the phase of source material. It was reported by kihlborg[2)] that the formation temperature by solid state reaction is 620～680°C for orthorhombic Mo_4O_{11}, 500～620°C for monoclinic Mo_4O_{11}, 600～780°C for monoclinic Mo_9O_{26} and 750～780°C for triclinic Mo_9O_{26}. Formation temperature of single crystals of each phase was the same. The photographs of some typical crystals are shown in Fig. 1～8. Single crystals of MoO_2 were polyhedral and about 2 mm in size, as shown in Fig. 1. Single crystals of Mo_4O_{11} shown in Fig. 2 and 3 were thin plate like with well-developed crystal face of (100). Developed crystal face of single crystal is (010) plane for Mo_8O_{23} (monoclinic) and monoclinic Mo_9O_{26}. Single crystals of triclinic Mo_9O_{26} were simultaneously grown at source zone and crystallization zone, as shown in Fig. 6 and 7 because temperature difference between the source zone and the crystallization zone was very small. Transport of

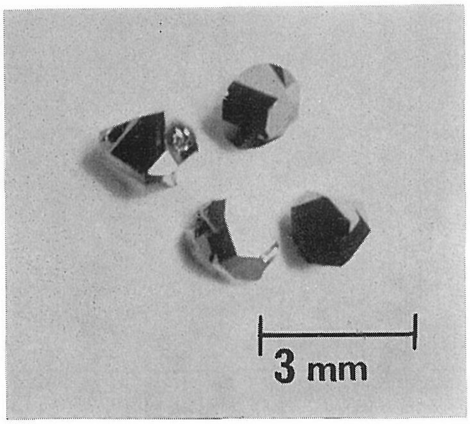

Fig. 1 MoO_2 crystals

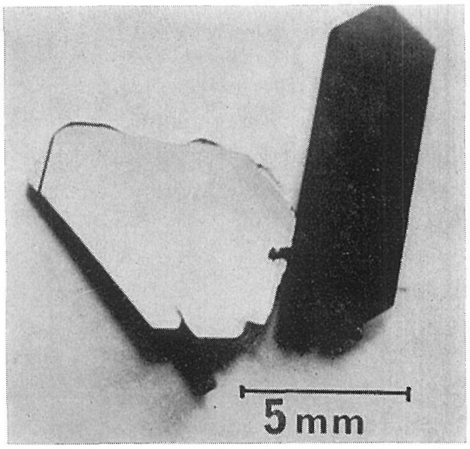

Fig. 2 Monoclinic Mo_4O_{11} crystals

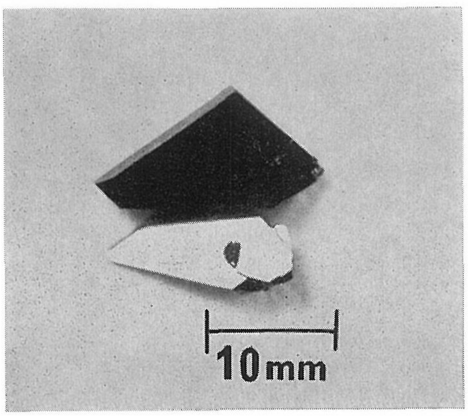

Fig. 3 Orthorhombic Mo_4O_{11} crystals

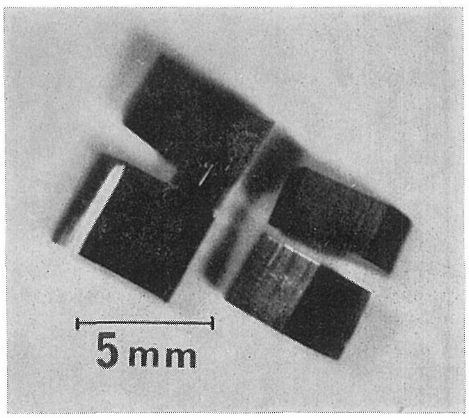

Fig. 4 Mo_8O_{23} crystals

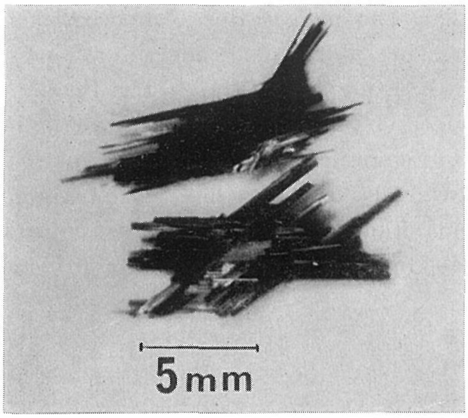

Fig. 5 Triclinic Mo_9O_{26} crystals

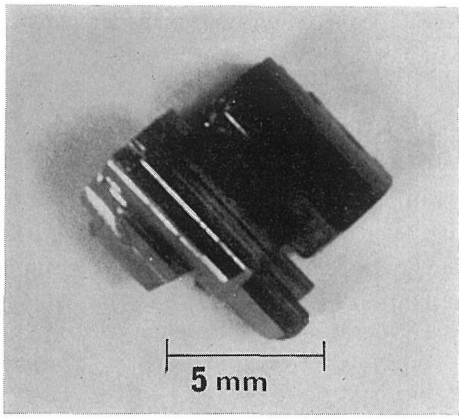

Fig. 6 Monoclinic Mo_9O_{26} crystals grown at crystallization zone

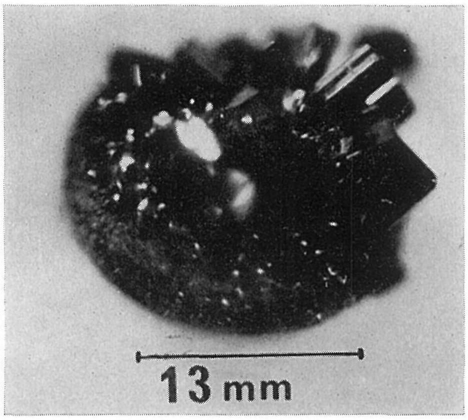

Fig. 7 Monoclinic Mo_9O_{26} crystals grown at source zone

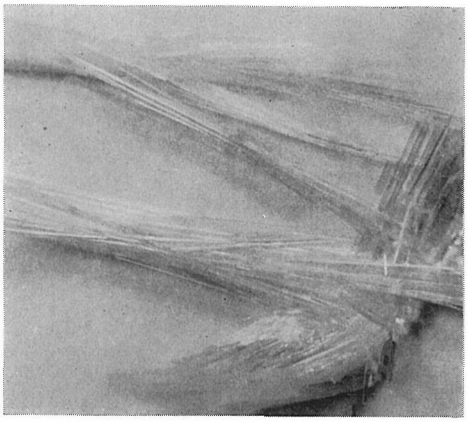

Fig. 8 MoO_3 crystals

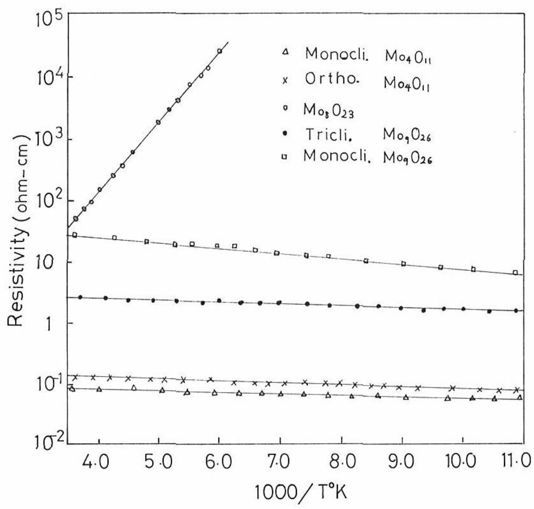

Fig. 9 Electrical resistivity-temperature curves of Mo_nO_{3n-1} single crystals

MoO_3 occurred without transport agent $TeCl_4$. This may be due to vaporization of MoO_3. The value of transport rate of MoO_3 in Table I shows the subtraction of the data due to vaporization of MoO_3 from the experimental data using $TeCl_4$.

Electrical resistivities of as-grown single crystals were measured from liquid nitrogen temperature to room temperature. Figure 9 shows the results of the electrical resistivity measurement. Intermediate oxides except triclinic Mo_9O_{26} were suggested to be metallic conductive in consideration of the value and the temperature dependence of resistivity. Triclinic Mo_9O_{26} showed semiconduction with the activation energy of 0.29 eV.

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